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PEI/Ag as an optical gas nano-sensor for intelligent food packaging

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***Abstract*—**In this work we report research carried out on the manufacturing of an optical sensor based on polyetherimide (PEI) and Ag nanoparticles (NPs) for food packaging and food freshness control applications. PEI/Ag films were fabricated and tested as optical sensors by exposing them to 0.01 M and 0.005 M of 2-mercaptoethanol (2-ME). Thiol groups of 2-ME react on the surface of the sample and reduce the silver ions to Ag NPs, which lead to the change of color. The real-time measurement of meat freshness was performed for salmon, chicken, turkey and beef. The colorimetric and UV-vis absorbance responses were measured over duration of 80 hours. The PEI/Ag sensor shows a good response to the released gases by meat. Moreover, salmon, chicken and turkey are shown to produce color changes of PEI/Ag films after 20 hours of exposure, and beef after 60 hours of exposure. Therefore, this nano-sensor has a potential to serve as an indicator of food spoilage in the packaging.

I. INTRODUCTION

Food safety is an emerging field that has received great attention due to increased public demands for health safety and food quality [1]. Intelligent food packaging is a solution that not only addresses food and storage quality, but also has the potential to reduce food waste. This type of packaging has a built-in sensor to monitor the safety of the product and informing the customers about the quality of the product [2]. In this work, PEI substrates were treated by silver ion exchange, which serve as a sensing surface for detection of 2-ME in vapor. PEI is a chemically inert plastic with excellent mechanical properties, which is widely used in 3-D printing by Fused Deposition Modeling and known under the name of ULTEM® [3]. Ag NPs have specific absorption wavelength and different colors in the visible range that could be used as a detection technique for optical colorimetric sensor. For the characterization of color change, it is proposed to employ portable UV-vis spectroscopy. UV-vis spectroscopy nano-sensors have received much attention due to their low cost, simple experimental set-up, portability, and direct analysis of the substrates from color changes [4]. The proposed PEI/Ag sensor is able to detect sulfur containing compounds, such as methyl mercaptan (CH_3SH), dimethyl sulfide ($(CH_3)_2S$), dimethyl disulfide (CH_3SSCH_3), and hydrogen sulfide (H_2S), that are released by spoiled meat, fish, milk and wine [5]. Therefore, volatile biogenic sulfides are the biomarkers, by which rotten meat can be identified. The amount of the sulfur containing compounds reflects freshness of the meat. The proposed sensor was tested as a proof of concept against the released gases from raw meat of chicken, turkey, beef, and salmon.

II. MATERIALS AND METHODS

A. Materials

PEI sheets (75 μm thick grade 1000B ULTEM®) were purchased from Cadillac Plastics, U.K. The 2-ME solution was purchased from Sigma Aldrich, U.K., and the rest of the chemicals were obtained from Fisher Scientific, U.K. The materials for sensor tests of salmon, chicken, turkey and beef were purchased from the local grocery store (Aldi™).

B. Methods

Silver-treated PEI substrates were prepared according to an earlier method reported in [6]. PEI sheets were cleaned with isopropanol prior to use and treated with 15 M KOH for 20 minutes with stirring at 50°C. The substrates were washed with de-ionized (D.I.) water for 2 minutes on each side and immersed into 0.1 M $AgNO_3$ for 20 minutes. After silver nitrate treatment, substrates were rinsed with D.I. water and dried. The modified surface of the PEI sheets serves as a sensor surface for the detection of 2-ME in vapor. Two concentrations of 2-ME were studied which are 0.01 M and 0.005 M. The set-up consists of a flask tube, filled with the 2-ME solution, as shown in Fig.1. The PEI/Ag sensor was inserted into a plastic tube and closed with a lid, while reacting with the vapors that are released by highly volatile 2-ME. The tubes were covered with aluminium foil to avoid the silver ions reduction under the ambient light. The reduction of silver ions and the formation of Ag NPs due to 2-ME binding were studied by measuring the optical absorbance using a portable DR 2800 spectrophotometer. This portable spectrophotometer takes up to four absorbance measurements in less than five seconds. The experimental set-up for monitoring meat freshness consists of the disposable plastic tube, shielded from the ambient light and loaded with the pieces of meat and, the sensor that is attached to a lid. The change of the color and absorbance responses of PEI/Ag

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sensor exposed to raw meat were checked every 20, 40, 60 and 80 hours and recorded by camera.

III. Results and Discussion

A. PEI/Ag as a sensor for 2-ME in vapour

2-ME is a chemical compound having an unpleasant odor of rotten fish due to the presence of thiol (-SH) organosulfur compound. Thiol has been long known for good chemisorption on the surface of metallic NPs such as silver and gold, forming stable metal-sulfur bonds [7], [8].

During the immersion of PEI into alkaline solution, O=C-N-C=O imide ring opens up allowing the adsorption of potassium ions. The following immersion of modified PEI to a silver nitrite solution results in the exchange of the potassium ions to silver ions [6]. When the PEI substrate with adsorbed silver ions is exposed to 2-ME, the organothiols can reduce silver ions to Ag NPs [9]. The change of the color of the PEI/Ag film and absorbance were monitored and recorded for three hours. The film changed color from transparent to yellow-brown once exposed to the 2-ME vapor.

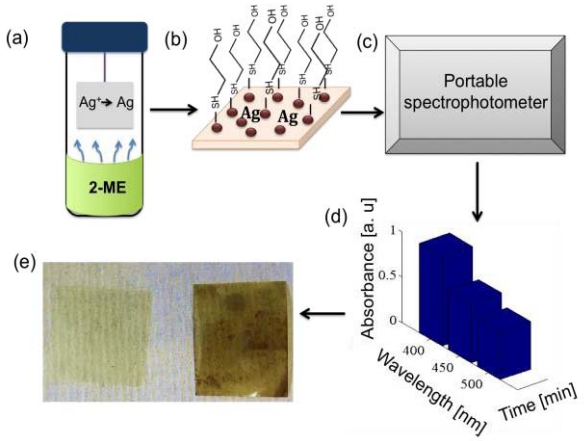

Fig. 1- A schematic of the sensor set up showing (a) a flask tube with PEI/Ag film exposed to 2-ME vapors, (b) chemisorption of thiols to Ag^+ prepared on PEI film, (c) a portable spectrophotometer, (d) expected absorbance results; (e) a photograph of the color change of PEI/Ag film from transparent to yellow-brown after 2-ME exposure.

Fig. 2 shows the UV-vis absorbance responses of PEI/Ag sensor exposed to 0.01 M and 0.005 M of 2-ME. We suggest that the thiol-silver interaction has led to the reduction of Ag^+ to Ag NPs, which corresponds to the change of the absorbance intensity. The absorbance that occurs at lower than 400 nm is due to PEI polymer [6]. For both 2-ME concentrations, the absorbance intensity increases with longer exposure times at the tested wavelengths. Since the absorbance of the solute depends on its concentration [10], [11] it implies that the Ag NPs concentration on the PEI substrate increases as Ag NPs react with the 2-ME molecules. The concentration of the formed Ag NPs on the PEI substrate reaches its maximum when the absorbance intensity plateaus with increasing exposure time. Therefore, the maximum Ag NPs concentration occurs after 30 minutes of exposure to 0.01 M of 2-ME and after 180 minutes for 0.005 M 2-ME.

The absorbance intensity increases for all tested wavelengths, indicating thereby the presence of rather a broad absorption band spectrum, due to a broad NPs size distribution and the presence of large particles (> 100 nm) [10], [12]. NPs size distribution could be also analyzed from the color change of the PEI/Ag once it reacted with 2-ME. The color of the optical sensor changes from light yellow to dark brown as exposure time propagates. Therefore, as color gets darker, the concentration of Ag NPs increases [13].

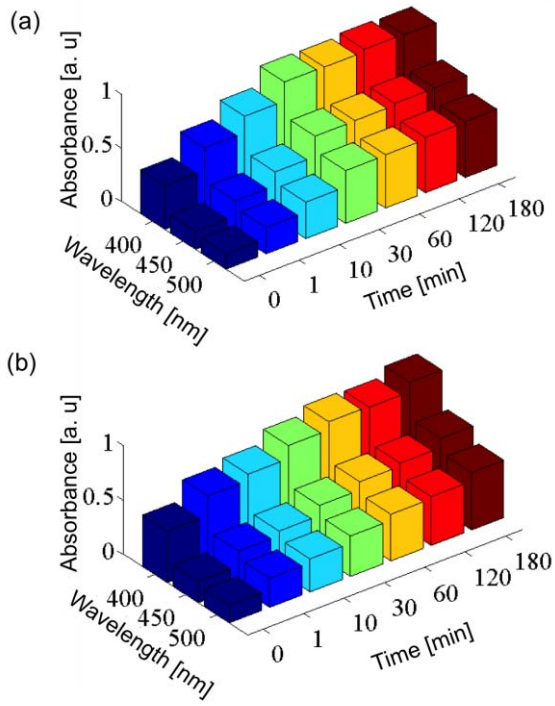

Fig. 2 –UV-vis absorbance response of the PEI/Ag sensor for different time of exposure and 2-ME concentrations (a) 0.01M, and (b) 0.005 M.

The binding kinetics could be analyzed from the real-time absorbance data. A net binding reaction rate mainly depends on the amount of available binding sites on the PEI/Ag substrate and concentration of the 2-ME analyte. Therefore, the reaction rate changes as the concentration of the 2-ME increases in the flask tube, while the number of binding sites on the substrate decreases leading to saturation. As the absorbance at lower than 400 nm is mostly due to PEI polymer, the peak intensity at 450 nm is taken as a response variable to a 2-ME concentration change. Fig. 3 shows a real-time kinetic response of PEI/Ag to 2-ME concentration solution of 0.01 M and 0.005 M as a function of absorbance intensity. The saturation curves were fitted by the two-phase exponential function using MATLAB (The MathWorks, Inc.):

$$A_t = Be^{k_1 t} + Ce^{k_2 t}, \quad (1)$$

Where A_t is intensity at a given time; B and C saturation intensity coefficients; k_1 and k_2 are binding constants. Fig.3 illustrates two fitting curves for 0.01 M and 0.005 M concentrations of 2-ME. The saturation equation coefficients for the PEI/Ag and 0.01 M 2-ME reaction are found with 95% confidence and computed as: B= 0.639 (a.u.), C = - 0.426 (a.u.), $k_1 = 4.17 \times 10^{-3}\ s^{-1}$, $k_2 = -5.07\ s^{-1}$. The coefficients of

the saturation equation for the reaction of PEI/Ag and 0.005 M 2-ME are computed with 95% confidence and calculated as: B= 0.471 (a.u.), C = - 0.219 (a.u.), k_1 = 107.76 x 10^{-3} s^{-1}, k_2 = - 18.17 s^{-1}. Therefore, the reaction of PEI/Ag with 2-ME has two binding constants and represented as k_1 – fast half-life and k_2 – slow half-life. The adsorption of 2-ME onto binding sites of PEI/Ag starts rapidly and then slows down reaching saturation, which implies that there are no binding sites left for the reaction to proceed. The response time for 0.01 M 2-ME is 25 times faster as for 0.005 M concentration. The rationale for this is that higher 2-ME concentration occupies PEI/Ag binding sites faster.

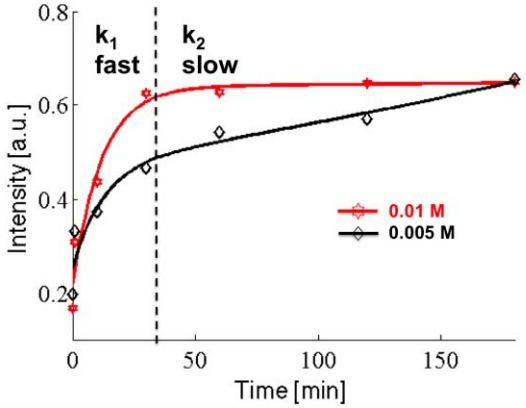

Fig. 3 – Fitting two-phase exponential curves for two concentrations of 2-ME: 0.01 M and 0.005 M. The curves describe an increase of the absorbance intensity as a function of the exposed time.

B. Real-time monitoring of meat freshness

Meat releases various volatile compounds once it gets spoilt such as S-containing compounds and various biogenic amines (cadaverine, putrescine, histamine) [5]. The release of these compounds has a characteristic odor. Fig. 4 shows the colorimetric responses of the sensor over exposed time to raw meat at room temperature (RT).

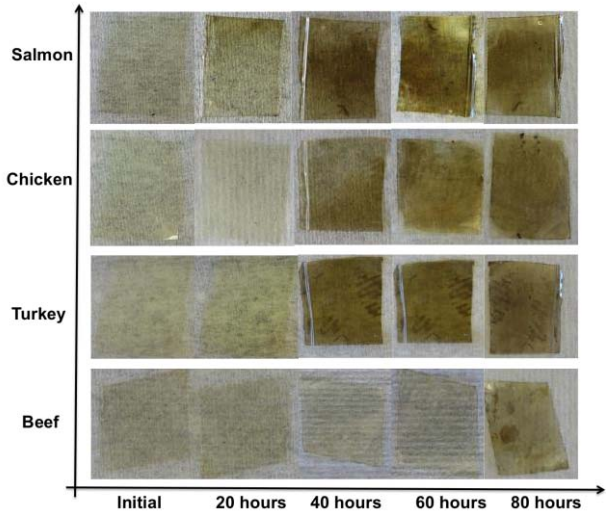

Fig. 4 - Colorimetric response of PEI/Ag sensor exposed to raw meat for 20, 40, 60 and 80 hours.

The color of the PEI/Ag film did not change during the first hours of the exposure. This may indicate that the gases released by fresh meat did not react with the sensor. However, over time, meat acquired a strong odor and gradual changes of the PEI/Ag film from transparent to yellow-brown were observed. Therefore, the observed color of the PEI/Ag sensor that is exposed to 2-ME vapors correlates with the color change of the PEI/Ag sensor, which is exposed to the vapors released by meat. PEI/Ag showed an evident response after 20 hours, when exposed to vapors that were getting released from spoiling salmon, chicken and turkey. Beef, in contrast, only showed a noticeable color change, when observed by eye after 60 hours of exposure. Fig. 5 shows UV-vis absorbance responses of the PEI/Ag optical sensor to the vapors released by rotten salmon, chicken, turkey and beef and, corresponding photographs of the experimental set-up.

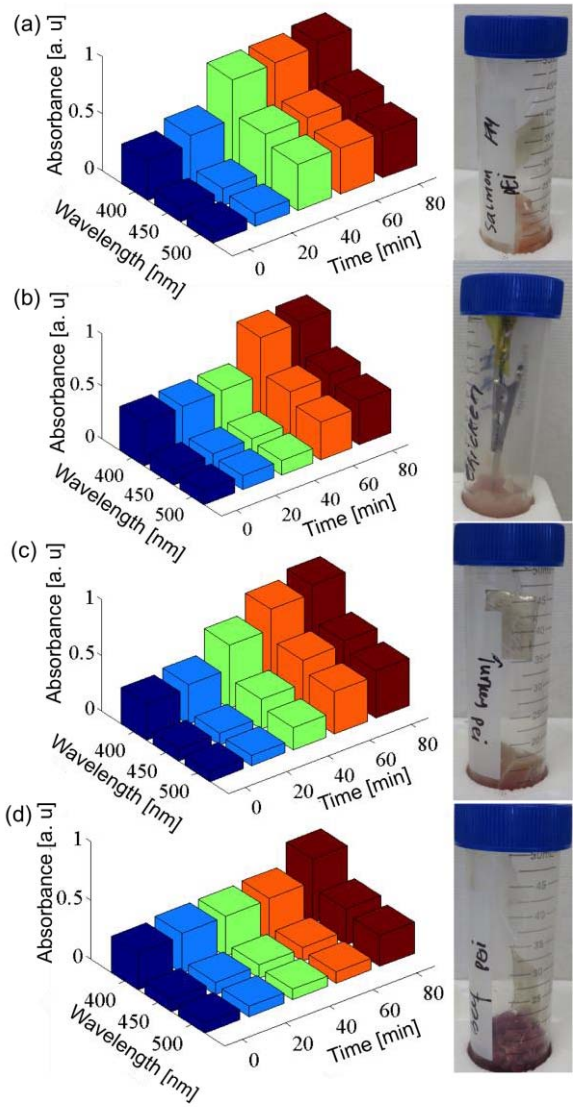

Fig.5 – UV-vis absorbance response and corresponding photographs of the PEI/Ag sensor for different exposure time to the vapors released by (a) salmon, (b) chicken, (c) turkey and (d) beef.

UV-vis spectroscopy correlates to the colorimetric response of PEI/Ag sensor. Thereby, the color change observed after 20 hours is represented as an increase of the absorbance peak intensity at 400 – 500 nm for all tested meat samples. As discussed earlier, the increase of the intensity peak correlates to the increase of the concentration of the reduced Ag NPs. Therefore, the increase of the NPs concentration can be related to the meat freshness. Thereby, as the absorbance peak intensity increases, the meat freshness decays.

There are a few possible ways to improve the response of the sensor. One way is to tune the size of the NPs. Smaller NPs will have an increased surface area and, therefore, an increased number of binding for the adsorption of the S-containing and biogenic amines. Another way is to minimize the PEI/Ag substrate size. Small PEI/Ag substrate size would result in less availability of the binding areas leading to faster saturation, which may speed up the sensor response. An advantage of such sensors is the usage of the 3-D printable PEI substrate, enabling printing different designs and geometries. This type of the sensor can be incorporated into the food packages and colorimetric response can be used as an indicator of meat spoilage. Furthermore, the sensor has potential for the reusability since the thermoplastic PEI is a recyclable material [14].

IV. Conclusion

A PEI/Ag sensor was developed for food freshness application. UV-vis absorbance response of the PEI/Ag was measured once the sensor was exposed to 2-ME in vapor. Two concentrations of 2-ME – 0.1 M and 0.005 M – show an increase of the absorbance peak intensity at 400 – 500 nm wavelengths, indicative of the reduction of the silver ions to silver NPs by capping with the thiol group. The resulting PEI/Ag optical sensor was also tested in a real-world environment by exposing it to raw meat such as salmon, chicken, turkey and beef. PEI/Ag shows a good colorimetric response after 20 hours of exposure for salmon, chicken, turkey and, after 60 hours for beef. Therefore, the proposed optical sensor has a potential for meat freshness monitoring and could be installed into intelligent food packaging.

Acknowledgment

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